New Synthetic Methodologies for Construction of Novel π-Extended Polycycles

博士論文

New Synthetic Methodologies for Construction of Novel π-Extended Polycycles

（新規 π 拡張縮環骨格構築法の開発）

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論文目次

Abstract

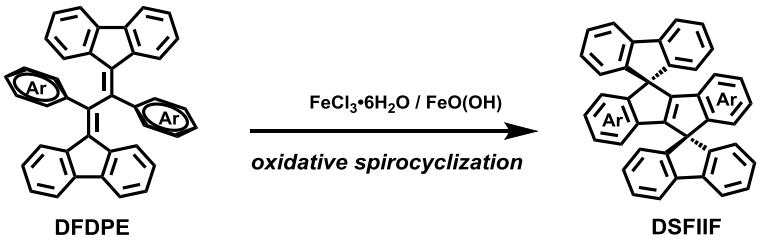
Introduction

π-Extended polycycles including polycyclic aromatic hydrocarbons (PAHs) and polycyclic (hetero)aromatic hydrocarbons have attracted significant attention for application in various organic electronics such organic field-effect transistors, organic light emitting diodes, and organic photovoltaics owing to their promising charge-carrier transporting property, light emitting performance, and narrow energy bandgap. Consequently, a variety of synthetic methodologies have been developed for constructing novel π-extended polycycles. Recently, we have been interested in developing new synthetic methodologies toward highly fused π-systems via C-H bond transformations.[1] The present doctoral dissertation focused on developing novel synthetic methods of π-extended polycycles in terms of single-electron oxidation of alkenes and consecutive C-H arylation.

Results and discussion

1. $FeCl_3$-Mediated Oxidative Spirocyclization of Difluorenylidene Diarylethanes Leading to Dispirocycles

Fluorene-based π-conjugated spirocycles have currently attracted a great attention as important optoelectronic materials in various fields of organic electronics due to their unique structural features. We report a novel $FeCl_3$-mediated oxidative spirocyclization for construction of a new class of di-spirolinked π-conjugated molecules, dispiro[fluorene-9,5′-indeno[2,1-*a*]indene-10′,9′′-fluorene]s (DSFIIFs) (eq. 1). The combination of $FeCl_3$ with FeO(OH) triggered an unprecedented double single-electron oxidation of difluorenylidene diarylethanes (DFDPEs) to afford the corresponding dispirocycles in high yields. The highest fluorescence quantum yield was up to 0.94 in solution. This protocol was also applicable to the synthesis of the non-spirolinked dihydroindenoindenes.[2]

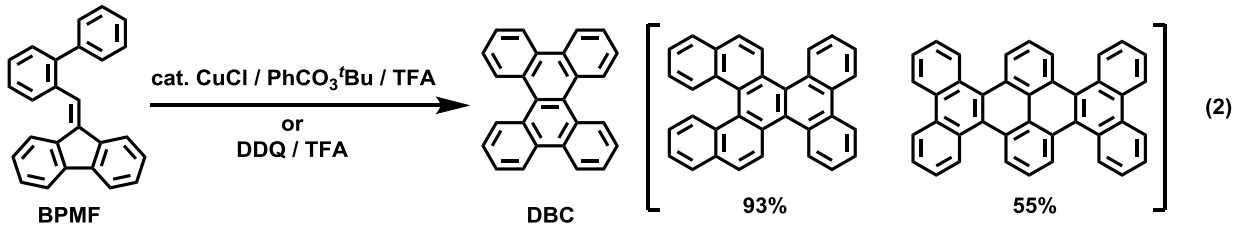


DFDPE DSFIIF (1)

2. Synthesis of Extended Polycyclic Aromatic Hydrocarbons (PAHs) by Oxidative Tandem Spirocyclization and 1,2-Aryl Migration

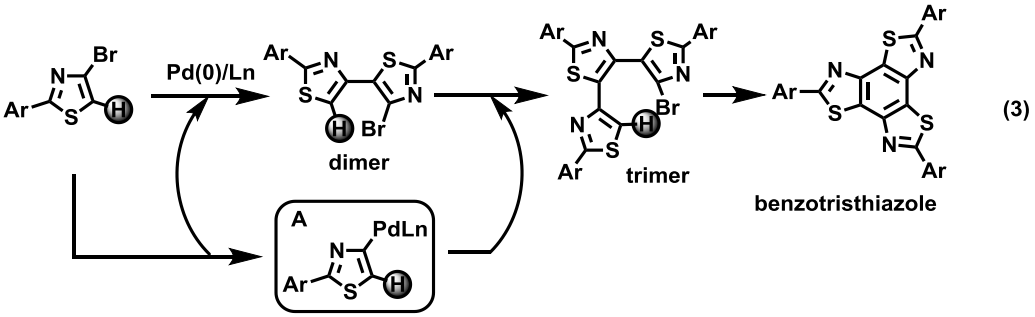
The extended polycyclic aromatic hydrocarbons (PAHs) have received significant interdisciplinary attention due to their semiconducting applications in diverse organic electronics as well as intriguing structural interests of well-defined graphene segments. We developed a highly efficient oxidative spirocyclization and 1,2-aryl migration tandem synthetic method for the construction of extended polyaromatic hydrocarbons (PAHs). The CuCl-catalyst/$PhCO_3{}^tBu$ or DDQ oxidation system in the presence of trifluoroacetic acid enables the selective single electron oxidation to take place preferentially at the more electron-rich alkene moiety of *o*-biphenylyl-substituted methylenefluorenes,

giving rise to the subsequent tandem process. A variety of extended PAHs involving functionalized DBCs, hexabenzotetracene, tetrabenzophenanthrotetraphene, tetrabenzophenanthropicene, and helicene derivatives have been readily synthesized in good to high yields without prefunctionalization of aromatic rings.



3. Synthesis of Benzotristhiazoles via Consecutive C-H Arylation Triggered Cyclotrimerization of 4-Bromothiazoles Catalyzed by Palladium

The π-extended star-shaped molecules with discotic polyaromatic or heteropolyaromatic units as central cores such as triphenylene, truxene, and triazatruxene offer a large π-surface to enhance the intermolecular charge transfer, facile self-assemble into columnar superstructure, strong fluorescence, and liquid crystallinity. We herein report a novel Pd-catalyzed cyclotrimerization of 4-bromo-2-arylthiazoles for constructing benzotristhiazoles with various peripheral π-conjugated arms (eq. 3). The thiazole-Pd species **A** generated from the optimal Pd(0)/XPhos catalyst systems enables the consecutive C-H arylation of 4-bromothiazoles, offering a unique approach for the construction of symmetric benzotristhiazoles with a wide range of π-conjugated functional groups that has never been reported to date.



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2. Zhao, J.; Xu, Z.; Oniwa, K.; Asao, N.; Yamamoto, Y.; Jin, T. *Angew. Chem. Int. Ed.* **2016**, *55*, 259.
3. Zhang, X.; Xu, Z.; Si, W.; Oniwa, K.; Bao, M.; Yamamoto, Y.; Jin. T. *Nat. Commun.* **2017**, *8*, 15073.